EFFECTS OF SURFACE CROSSING IN CHEMICAL REACTIONS: THE H_3^+ SYSTEM

Richard K. Preston and John C. Tully*
Department of Chemistry
Yale University
New Haven, Connecticut, 06520

ABSTRACT

Approximate potential energy surfaces for the two lowest singlet states of H_3^+ are calculated using a Cashion-Herschbach approach. The non-adiabatic terms which couple these surfaces can be directly computed in this approximation. From the magnitudes of these coupling terms it is apparent that, for excitation energies below about 10 eV, non-adiabatic transitions must be confined almost entirely to a region localized at the avoided crossing of the two surfaces. This fact suggests the following simplified picture of the dynamics of the $H^+ + H_2$ reaction: As the H^+ and H_2 in a low vibrational state approach, they remain on the lower potential surface (there is no initial electron jump). They continue to adiabatically follow the lower surface in the close-collision region, so the probability of a non-adiabatic transition does not appear to be related to the lifetime of the collision complex. It is while the products are receding that electronic transitions become important. Consequences of this model on the threshold for formation of H_2^+ and on the partition of vibrational energy in the products are discussed, and a comparison with recent experiments of Krenos and Wolfgang is included.

I. INTRODUCTION

The reaction

$$H^+ + H_2 \rightarrow H_2 + H^+, \quad \Delta H = 0 \qquad (1a)$$

$$H^+ + H_2 \rightarrow H_2^+ + H, \quad \Delta H = 1.835 \text{ eV}, \qquad (1b)$$

as well as many of its deuterium isotopic variations, has recently been investigated experimentally. Cross-sections and product translational energy distributions have been measured as a function of initial collision energy by Krenos and Wolfgang,[1] and by Holliday, Muckerman and Friedman.[2]

These reactions are of fundamental importance because they provide an excellent opportunity for direct, meaningful comparison between experiment and theory. H_3^+ is a two-electron system for which it is presently feasible to perform accurate ab initio calculations of potential energy surfaces.[3] In spite of this simplicity, however, these reactions exhibit features such as charge transfer, rearrangements and dissociation that are important in the most complicated chemical reactions.

Csizmadia, Polanyi, Roach and Wong[4] have recently reported a three-dimensional classical trajectory calculation of the dynamics of the reaction

$$D^+ + H_2 \rightarrow H^+ + HD, \qquad (2)$$

using the ab initio potential surface of reference 3. This calculation was performed for center-of-mass collision energies of 3, 4.5 and 6 eV. Unfortunately, this study is of limited value because it does not take into account non-adiabatic interaction with a second potential energy surface. This interaction can be seen from experiment to be very important because at energies above its threshold the observed cross-section of channel (1b) is roughly equal to that of (1a).[1,2]

The reason that there exists such a strong interaction between the two surfaces can be seen from Fig. 1,[5] which plots the potential energy curves for the ground states of H_2 and H_2^+ with a common asymptote. We can define a configuration of H_3^+ by specifying the coordinates R_1, R_2 and R_3, the distances between nuclei a and b, b and c, and a and c, respectively. The curves of Fig. 1 can then be thought of as slices of the lowest H_3^+ potential surfaces for configurations $R_2=R_3=\infty$; i.e., one curve corresponds to H_2 plus asymptotically distant H^+ and the other to H_2^+ plus asymptotically distant H. As is shown in Fig. 1, these curves cross at $R_1\approx 2.5$ a.u. If the third nucleus is now brought closer (R_2 and R_3 large but finite), the state correlating with H_2^+ plus H splits into two surfaces, a singlet and a triplet ($^1\Sigma^+$ and $^3\Sigma^+$ in linear configurations). The surface correlating with H_2 plus H^+ is also $^1\Sigma^+$ in linear configurations, and so the crossing of the two singlet surfaces becomes avoided. As a result, each of these surfaces has regions for which the electronic configuration

is approximately that of H_2+H^+ and other regions for which it is approximately that of H_2^++H. It is this avoided crossing that is responsible for the large probability of formation of channel (1b).[6]

In the present paper we discuss in more detail the nature of the two important potential surfaces and of their non-adiabatic coupling. We then reexamine the dynamics of reaction (1) in the 0-10 eV collision energy range. Using qualitative arguments, we make several predictions about its mechanism, as well as a preliminary comparison with experiment. We shall report quantitative results in a future paper.[7]

II. THE POTENTIAL SURFACES

In order to accurately describe reaction (1), it is necessary to possess knowledge of the lowest two singlet electronic states of H_3^+, and the non-adiabatic coupling between these states. The Born-Oppenheimer electronic states of H_3^+ have been the object of several extensive ab initio calculations.[3,8,9] As a result of this work, the ground electronic surface is known quite accurately. However, the lowest excited singlet state has been computed for only a few nuclear configurations,[8,10-12] and calculations of the magnitude of the coupling between these surfaces due to nuclear motion has not previously been reported.

We have chosen to compute the potential surfaces by a very approximate method based on the London approach. The coulomb

and exchange integrals that arise are computed using the method of Cashion and Herschbach.[13] Thus, we designate this the LCH approach.[14] This method has several advantages in addition to its simplicity.[15] It expresses the electronic structure of H_3^+ in terms of the electronic structures of the fragments of which it is composed, $H_2 + H^+$ and $H_2^+ + H$; i.e., it uses directly just those configurations which we intuitively know are responsible for the crossing of the surfaces in this system. Secondly, it allows the non-adiabatic coupling terms to be calculated in a very straightforward way (see Sec. III). The dangers involved in using an approximate, non-variational method of this type are very real. However, these dangers are substantially minimized for this system because of the availability of accurate variational calculations of both of the electronic states of interest. The validity of the LCH results can be directly tested by comparison with accurate calculations at those nuclear configurations for which the latter are available.

Using the LCH method, the two energy levels of interest are simply the lowest two eigenvalues of a symmetric 3x3 matrix given by[17]

$$H_{11} = E_1 + ({}^gE_2 + {}^uE_2 + {}^gE_3 + {}^uE_3)/2 - 2E_H$$

$$H_{12} = ({}^gE_3 - {}^uE_3)/2 \qquad (3)$$

$$H_{13} = ({}^gE_2 - {}^uE_2)/2$$

$$H_{22} = E_2 + ({}^{g}E_1 + {}^{u}E_1 + {}^{g}E_3 + {}^{u}E_3)/2 - 2E_H$$

$$H_{23} = ({}^{g}E_1 - {}^{u}E_1)/2$$

$$H_{33} = E_3 + ({}^{g}E_1 + {}^{u}E_1 + {}^{g}E_2 + {}^{u}E_2)/2 - 2E_H.$$

E_1 is the electronic energy of the ${}^1\Sigma_g^+$ ground state of H_2, evaluated at internuclear distance R_1. ${}^{g}E_1$ and ${}^{u}E_1$ are the energies of the ${}^2\Sigma_g^+$ ground state and ${}^2\Sigma_u^+$ first excited state of H_2^+, respectively, evaluated at R_1. E_H is the energy of the 1S state of H, -.5 a.u. The analytic functions of Pedersen and Porter were used to compute the values of E_1, ${}^{g}E_1$ and ${}^{u}E_1$.[18]

The form of the attractive ground state potential, as calculated by the LCH method, is shown for linear configurations in Fig. 2. The minimum energy for linear configurations is -1.299 a.u. located at $R_1=R_2=R_3/2=1.53$ a.u. Conroy[8] computed a value of -1.280 a.u. at $R_1=R_2=R_3/2=1.54$ a.u. The lowest point on the ground state surface occurs in an equilateral configuration, for which the LCH method gives an overall minimum at $R_1=R_2=R_3=1.73$ a.u. with an energy of -1.356 a.u. Conroy[8] obtained a value of -1.348 a.u. at $R_1=R_2=R_3=1.65$ a.u.

The first excited singlet state computed by the LCH approach is a typical repulsive potential. The same result was found by a number of earlier calculations for the few configurations for

which numbers were reported.[8,10-12] Fig. 3 shows an energy contour of the linear configurations. It has the same general shape as the ground state of H_3. The saddle point is located at $R_1=R_2=R_3/2=3.0$ a.u. The energy of the saddle point is 2.17 eV above that of separated $H_2^+ + H$ (4.13 eV above separated $H_2 + H^+$). Conroy[8] has reported points on this surface at some C_{2v} configurations. The agreement for this state is not as good as for the ground state.[19] Conroy[8] obtained -0.968 a.u. compared to the LCH result of -1.014 a.u. at $R_1=R_2=R_3/2=2.5$ a.u. For the equilateral configuration $R_1=R_2=R_3=3.0$ a.u., he reported an energy of -0.908 a.u. compared to the LCH result of -0.901 a.u.

The separation between the two surfaces is found to be largest in equilateral configurations and smallest in linear configurations. The non-adiabatic coupling between the states is correspondingly greatest for linear configurations.

For equilateral configurations, the symmetry of the first excited singlet is $^1E'$; it becomes degenerate with another excited state which is associated with the third eigenvalue of the matrix (3). This is an example of a conical intersection as discussed by Teller,[20] but since this crossing lies above the limit for 3 body dissociation it must play a very small role in the dynamics of reaction (1). The avoided surface crossing responsible for the appearance of channel (1b) is not of this type. It can be pictured in Fig. 4. The two solid lines are slices of the linear potential surfaces of Figs. 2 and 3 taken at $R_1=5$ a.u. Comparison

with Fig. 1 shows that as the third body is brought closer, the degeneracy at $R \simeq 2.5$ is removed. Therefore, for large R_1 one would expect trajectories to follow diabatic curves which look similar to those of Fig. 1. For smaller R_1, as the surfaces separate, low energy trajectories should have a greater tendency to follow adiabatic curves like those pictured in Fig. 4.

III. NON-ADIABATIC COUPLING

In order to determine at what point this transition between diabatic and adiabatic behavior occurs, and indeed to what extent such a simplified picture is valid at all, it is necessary to consider the off-diagonal coupling between the two adiabatic surfaces. The total Hamiltonian H for the system is the sum of the clamped nuclei part, H_o, and the nuclear kinetic energy operator, T_N:

$$H = T_N + H_o, \tag{4}$$

where

$$T_N = -\sum_N \left[\frac{1}{2m_N} \nabla_N^2\right] \tag{5}$$

The usual adiabatic electronic wave functions $\phi_i(\underset{\sim}{R};\underset{\sim}{r})$ are eigenfunctions of H_o:

$$[H_o - E_i(\underset{\sim}{R})]\phi_i(\underset{\sim}{R};\underset{\sim}{r}) = 0, \tag{6}$$

where $\underset{\sim}{r}$ refers to electronic coordinates and $\underset{\sim}{R}$ to nuclear coordinates.

Let us now obtain eigenfunctions of the total Hamiltonian (4) in the two-state approximation; i.e., we choose the total wave function $\Psi(\underset{\sim}{R},\underset{\sim}{r})$ to be of the form

$$\Psi(\underset{\sim}{R},\underset{\sim}{r}) = \chi_1(\underset{\sim}{R})\phi_1(\underset{\sim}{R};\underset{\sim}{r}) + \chi_2(\underset{\sim}{R})\phi_2(\underset{\sim}{R};\underset{\sim}{r}). \tag{7}$$

Operating on Ψ with (4) and multiplying from the left by $\langle\phi_j(\underset{\sim}{R};\underset{\sim}{r})|$, $j=1,2$, results in two coupled equations for the nuclear wave functions $\chi_i(\underset{\sim}{R})$:[21]

$$[H_{11}-E_1]\chi_1(\underset{\sim}{R}) = \sum_N \langle\phi_1(\underset{\sim}{R};\underset{\sim}{r})|\nabla_{\underset{\sim}{N}}|\phi_2(\underset{\sim}{R};\underset{\sim}{r})\rangle\cdot\frac{1}{m_N}\nabla_{\underset{\sim}{N}}\chi_2(\underset{\sim}{R}) \tag{8a}$$

$$[H_{22}-E_2]\chi_2(\underset{\sim}{R}) = \sum_N \langle\phi_2(\underset{\sim}{R};\underset{\sim}{r})|\nabla_{\underset{\sim}{N}}|\phi_1(\underset{\sim}{R};\underset{\sim}{r})\rangle\cdot\frac{1}{m_N}\nabla_{\underset{\sim}{N}}\chi_1(\underset{\sim}{R}). \tag{8b}$$

Here we have used the relation

$$\langle\phi_1(\underset{\sim}{R};\underset{\sim}{r})|\nabla^2|\phi_2(\underset{\sim}{R};\underset{\sim}{r})\rangle = 0\ , \tag{9}$$

which is easily shown to be valid in the strict two-state approximation as a consequence of choosing the ϕ's to be real and normalized. The terms on the rhs of Eqs. (8) responsible for

coupling the two adiabatic states depend on the nuclear velocities, $\frac{1}{m_N}\nabla_N \chi_i$, multiplied by matrix elements of the form

$$\langle \phi_1 | \frac{\partial \phi_2}{\partial R} \rangle = -\langle \phi_2 | \frac{\partial \phi_1}{\partial R} \rangle \ . \tag{10}$$

In the LCH approach one implicitly expresses the electronic wave functions ϕ_j in terms of undetermined basis functions u_i, which are assumed to be orthogonal (neglect of overlap):

$$\phi_j = \sum_i C_{ij} u_i \tag{11}$$

The off-diagonal matrix elements (10) can be expressed in terms of these functions:

$$\langle \phi_1 | \frac{\partial \phi_2}{\partial R} \rangle = \sum_i C_{i1} \frac{dC_{i2}}{dR} + \sum_{i,j} C_{i1} C_{j2} \langle u_i | \frac{du_j}{dR} \rangle . \tag{12}$$

Consistent with neglect of overlap, we set

$$\langle u_i | \frac{du_j}{dR} \rangle = 0, \qquad i \neq j . \tag{13}$$

For u_i real and normalized, relation (13) is true for i=j as well, so

$$\langle \phi_1 | \frac{\partial \phi_2}{\partial R} \rangle = \sum_i C_{i1} \frac{dC_{i2}}{dR} \tag{14}$$

These terms can easily be calculated from derivatives of matrix elements of the LCH Hamiltonian (3):

$$\langle\phi_1|\frac{\partial\phi_2}{\partial R}\rangle = \langle\phi_1|D|\phi_2\rangle/[E_2-E_1] \ , \tag{15}$$

where the matrix D is defined by

$$D_{ij} = \frac{\partial}{\partial R} H_{ij} \ , \tag{16}$$

and we have used the relation $[H_o-E_i]\phi_i=0$.

Since we have expressed H_{ij} in analytic form (Eq. 3), we can easily obtain D_{ij} in analytic form. The obvious simplicity of this method in comparison with numerical procedures suggests that this and related approaches might be extremely valuable in obtaining a semi-quantitative understanding of non-adiabatic effects in many more complicated systems.[22]

The dashed line of Fig. 4 is the matrix element $\langle\phi_1|\frac{\partial\phi_2}{\partial R_2}\rangle_{R_1=5 \text{ a.u.}}$. Figures 5 and 6 show contour maps of the matrix elements $\langle\phi_1|\frac{\partial\phi_2}{\partial(R_1+R_2)}\rangle$ and $\langle\phi_1|\frac{\partial\phi_2}{\partial(R_1-R_2)}\rangle$, respectively.[23] It can immediately be seen from these figures that the coupling terms are very large only at the avoided crossing (R_1 or $R_2\simeq 2.5$ a.u.), and for very small values of R_1 or R_2. In the region of the crossing ($R_2\simeq 2.5$ a.u., $R_1\gtrsim 5$ a.u.) the element $\langle\phi_1|\frac{\partial\phi_2}{\partial R_2}\rangle$ becomes very large;

$\langle\phi_1|\frac{\partial\phi_2}{\partial R_1}\rangle$ remains relatively small. Therefore it is vibrational motion, not translational, that is most effective in producing non-adiabatic transitions.

To obtain a rough quantitative idea of the relation between the magnitude of the coupling term (10) and the resulting probability of non-adiabatic transition, we can make use of the Massey parameter:[24]

$$w = |E_1-E_2|/[V\langle\phi_1|\frac{\partial\phi_2}{\partial R}\rangle] \ . \qquad (17)$$

$w>>1$ is the condition for weak coupling. For the H_3^+ system the separation between the two electronic surfaces $|E_1-E_2|$ can vary between 0 and 1 a.u. in the regions of interest. Taking a typical value of .03 a.u. and setting the velocity V=.01 a.u. (2×10^6 cm/sec, corresponding to kinetic energies of a few volts) we find for $\langle\phi_1|\frac{\partial\phi_2}{\partial R}\rangle=1$ that w=3; i.e., roughly speaking for $\langle\phi_1|\frac{\partial\phi_2}{\partial R}\rangle\gtrsim1$ a.u. the coupling is strong enough to induce non-adiabatic transitions with singificant probability. For $\langle\phi_1|\frac{\partial\phi_2}{\partial R}\rangle$ <1 a.u., non-adiabatic transitions are relatively unlikely at energies of only a few eV.

IV. DISCUSSION

Even without performing calculations on the dynamics of reaction (1) we can obtain some qualitative insight into its mechanism.[7] In any system such as this for which two or more

adiabatic electronic potential surfaces are known to interact strongly, there exists the possibility that the nuclei cannot be described even approximately as moving on any one potential surface at any given instant (with perhaps occasional jumps between surfaces). Rather the nuclei might experience an effective potential which is not associated with a single surface but is some kind of average. This would be expected to be true if the coupling terms remained significant over a large region of configuration space. It could be the case even below the threshold for formation of electronically excited products if the upper surface(s) has attractive regions or if "virtual transitions" to classically forbidden regions of an upper surface were important. In the H_3^+ system the small masses of the nuclei make such a situation seem more likely. However, from Figs. 5 and 6 we see that, excluding regions of very small R, the coupling terms are large only along a line[25] localized at the avoided crossing. Thus it seems likely that away from this crossing seam where the non-adiabatic effects are quite small, for low energy collisions, the motion of the nuclei can be treated to a reasonable approximation quasi-classically on one or the other potential surface. It is this approximation and not the accuracy of the individual surfaces that may well turn out to be the limiting factor in obtaining accurate trajectories that proceed through the dotted or crossed hatched areas of Figs. 5 and 6. The extent to which this is true is presently being examined quantitatively.[26]

In light of this, the mechanism of reaction (1) can be visualized in the following way. If H_2 is initially in a low vibrational state ($v \leq 4$) then its vibrational amplitude will be insufficient to reach the crossing seam, and therefore non-adiabatic transitions should not occur as the H^+ and H_2 approach at large distances; i.e., an initial electron jump is very improbable. (Charge transfer at large distances could occur if H_2 was initially excited above the $v=4$ level.) The regions of large coupling at small internuclear separations are not energetically accessible for collision energies below 10 eV, so as the particles collide they are still unlikely to undergo a non-adiabatic transition. Similarly, as the nuclei move in the region of the deep potential well of the lower surface, they should follow that surface adiabatically. This can be seen from the size of the coupling terms in Figs. 5 and 6.[27] This is chiefly a reflection of the fact that for those configurations for which the lower energy surface is very attractive, the upper surface is correspondingly repulsive. Therefore the two surfaces have a large energy separation and small interaction in this region. In fact, a large part of the upper surface in this region is classically forbidden for collision energies below about 5 eV. Thus it appears probable that, contrary to the suggestion of Holliday, et.al.,[2] the lifetime of the collision complex has little to do with the likelihood of occurrence of an internal conversion. Rather, the electronic configuration of the products, channel (1a) vs. (1b), is determined as the products

separate and move back and forth through the crossing seam. The question of whether or not the reaction does in fact involve a long-lived intermediate cannot be answered without detailed calculations.

The quasi-classical trajectory calculations of Csizmadia, et.al.[4] considered motion on the ground state surface alone, and were restricted to the description of the thermoneutral product (2) only. Such a calculation should be accurate for collision energies below about 2.2 eV because the trajectories could not reach the crossing seam. In the range 3 to 6 eV for which their calculations were carried out, however, the calculations are not meaningful even for the description of the thermoneutral channel (2). This is due to the fact that after collision, as the separation between products increases, trajectories should follow a diabatic rather than an adiabatic surface when passing through the seam. But this breakdown of the calculation occurs only when the products are receding. Before product separation trajectories should, except for rare cases, evolve essentially entirely on the lower surface. Therefore the conclusions of Csizmadia, et.al.[4] as to the complex vs. direct nature of the reaction mechanism should be meaningful, even at energies of 3 to 6 eV.

Because the upper surface is repulsive, the crossing seam achieves its lowest energy in the asymptotic region. Therefore we can make some predictions concerning the H_2^+ reaction threshold and the partitioning of vibrational energy in the products, based

on the asymptotic potential curves shown in Fig. 1.[28] In order for H_2^+ product to be formed with significant probability, the system must have enough energy to reach the crossing seam. As shown in Fig. 1, this effectively requires that there be enough energy to form H_2^+ in its v=1 state. This results in a predicted threshold for reaction (1b) of 2.106 eV, rather than 1.835 eV obtained from thermodynamic considerations.

Now consider reaction (1) as the initial energy is increased from below to above the threshold for formation of H_2^+. The H_2 produced in the initial close collision with vibrational quantum number ≤ 4 should not be affected much by the opening of the new channel, because their vibrational amplitude is not large enough to reach the crossing seam. Note that, as shown in Fig. 1, the v=4 level lies above the v=0 level of H_2^+ but not above the crossing energy. H_2 formed with $v>4$ can reach the crossing and should be depleted by competition with the H_2^+ channel. Thus H_2 should be formed with predominantly low vibrational energy. Similarly, virtually no H_2^+ should be formed with v=0. Furthermore, from dynamic considerations it is expected that very little H_2^+ will be formed in the v=1 level.[29]

Recently in this laboratory Krenos and Wolfgang[30] have measured the velocity distribution of H_2^+ formed in reaction (1). Fig. 7 compares their experimental H_2^+ product velocity distribution to two distributions obtained by the phase space theory.[31,32] In one of the phase space calculations all energetically accessible vibrational levels were included, while in the second the v=0 and

v=1 states were omitted. It can be seen that the agreement is better if the v=0 and v=1 levels are left out of the calculation, suggesting that H_2^+ is indeed formed with vibrational energy higher than that which would be expected from statistical arguments.[33]

These predictions have been based on the assumption that the H_3^+ system does involve a localized avoided surface crossing rather than strong non-adiabatic coupling over a large region of configuration space. If this assumption is valid, as is indicated by Figs. 5 and 6, then it suggests that the dynamics of reaction (1) can be treated by an extension of the quasi-classical trajectory approach. The motion of the nuclei would be described by a classical trajectory on the initial potential surface until it reached the crossing seam. At this point a decision would be made as to whether or not the system jumped to the other surface, according to a probability function $P(\underset{\sim}{R},\underset{\sim}{V})$. The trajectory would then be continued classically on whichever surface was indicated, with a small velocity correction if it did switch surfaces, until it again reached the seam. The probability function $P(\underset{\sim}{R},\underset{\sim}{V})$ would depend, in general, on position $\underset{\sim}{R}$ and velocity $\underset{\sim}{V}$. It could be chosen in any of a number of ways such as a simple step function (P=1 or 0), a Landau-Zener type expression or perhaps even by actual numerical integration of the coupled equations through the seam. Calculations along this line are currently being carried out in conjunction with a study of the validity of this approach.[26]

ACKNOWLEDGMENTS

This work was supported by the National Aeronautics and Space Administration, contract NGR07-004-043. The authors are grateful to Mr. John Krenos and Professor Richard Wolfgang for many interesting discussions, as well as for permission to quote their experimental results prior to publication. RKP would like to thank Dr. Buddy Bruner for many useful discussions. JCT wishes to acknowledge the National Science Foundation for their support of the initial stages of this work in the form of a postdoctoral fellowship.

FOOTNOTES

*Present address: Bell Telephone Laboratories, Murray Hill, New Jersey, 07974.

1. J. Krenos and R. Wolfgang, J. Chem. Phys. 52, 5961 (1970).
2. M.G. Holliday, J.T. Muckerman and L. Friedman, to be published.
3. An accurate ab initio calculation of the ground state of H_3^+ at 250 nuclear configurations has recently been carried out by I.G. Csizmadia, R.E. Karl, J.C. Polanyi, A.C. Roach and M.A. Robb, J. Chem. Phys. 52, 6205 (1970).
4. I.G. Csizmadia, J.C. Polanyi, A.C. Roach and W.H. Wong, Can. J. Chem. 47, 4097 (1969).
5. The crossing of these surfaces has been pointed out by H. Conroy, ref. 8.
6. We have assumed in this paper that spin-orbit coupling in H_3^+ is sufficiently small that the triplet surface cannot play an important role in reaction (1). The validity of this assumption should be investigated quantitatively.
7. J.C. Tully, R.K. Preston and R. Wolfgang, to be published.
8. H. Conroy, J. Chem. Phys. 51, 3979 (1969).
9. For a discussion of earlier studies of this system see M.E. Schwartz and L.J. Schaad, J. Chem. Phys. 47, 5325 (1967).
10. J.O. Hirschfelder, J. Chem. Phys. 6, 795 (1938).
11. R.E. Christoffersen, J. Chem. Phys. 41, 960 (1964).
12. A. Wu and F.O. Ellison, J. Chem. Phys. 48, 1491 (1968).
13. J.K. Cashion and D.R. Herschbach, J. Chem. Phys. 40, 2358 (1964).

14. This method could just as well be called the diatomics-in-molecule with zero overlap, for the two methods are equivalent as has been pointed out by F.O. Ellison, J. Chem. Phys. 41, 2198 (1964).

15. When applied to H_3^+, more involved approaches such as the method of Porter and Karplus (see ref. 16) are in worse agreement with ref. 8 than the zero overlap methods.

16. R.N. Porter and M. Karplus, J. Chem. Phys. 40, 1105 (1964).

17. F.O. Ellison, N.T. Huff and J.C. Patel, J. Am. Chem. Soc. 85, 3544 (1963).

18. L. Pedersen and R.N. Porter, J. Chem. Phys. 47, 4751 (1967).

19. The agreement between the LCH results and more accurate calculations of the excited surface is particularly poor for configurations involving small internuclear distances. However, this is unimportant for the description of reaction (1) because of the repulsive nature of this surface which results in these configurations being classically forbidden for collision energies below 10 eV or so. In the classically allowed regions the agreement between DIM and more accurate calculations is quite good.

20. E. Teller, J. Phys. Chem. 41, 109 (1937). See also G. Herzberg and H.C. Longuet-Higgins, Disc. Faraday Soc. 35, 77 (1963).

21. Bras and kets indicate integration over electronic coordinates $\underset{\sim}{r}$ only. Equations (8) are the usual two-state equations for the optimum scattering function of the form (7) according to

the Köhn variational principle. See W. Köhn, Phys. Rev. 74, 1763 (1948).

22. It is important to note that the matrix elements (10) can be obtained in this way without explicit knowledge of the basis functions u_i. Approximate methods such as LCH are generally reasonably successful in predicting properties which do not depend explicitly on the (unknown) basis functions, but are often seriously in error when calculating properties for which actual expressions for the basis functions are required.

23. The coordinates R_1+R_2 and R_1-R_2 were chosen simply to make the figures symmetrical.

24. See, for example, E.E. Nikitin, in Chemische Elementarprozesse, edited by H. Hartmann (Springer-Verlag, Berlin and Heidelberg, 1968).

25. A surface in three dimensions.

26. J.C. Tully and R. Preston, to be published.

27. Note that, as mentioned earlier, the magnitude of the coupling decreases as the geometry is bent away from linear.

28. Partitioning of rotational energy in the products of reaction (1) is discussed by D.R. Herschbach, K. Lacmann, J. Tully and R. Wolfgang, to be published.

29. In order for H_2^+ to be formed the system must undergo an odd number of non-adiabatic transitions. For trajectories which just cross the seam this is expected to be unlikely.

30. J. Krenos and R. Wolfgang, to be published.

31. See J.C. Light, Disc. Faraday Soc. 44, 14 (1968), and references therein.

32. To more easily compare with experiment, the phase space calculations were "smoothed" to eliminate vibrational structure.

33. Experiments are currently being carried out on this reaction which might be capable of resolving H_2^+ vibrational structure (Private communication with J. Krenos and R. Wolfgang). This would provide an even more stringent test of the theory.

FIGURE CAPTIONS

Fig. 1 Potential curves of the ground states of H_2 and H_2^+, drawn with the same asymptote, showing the crossing at R≈2.5 a.u.

Fig. 2 Potential energy surface for the ground state of linear H_3^+. R_1 and R_2 are in a.u. and energies in eV relative to dissociated particles.

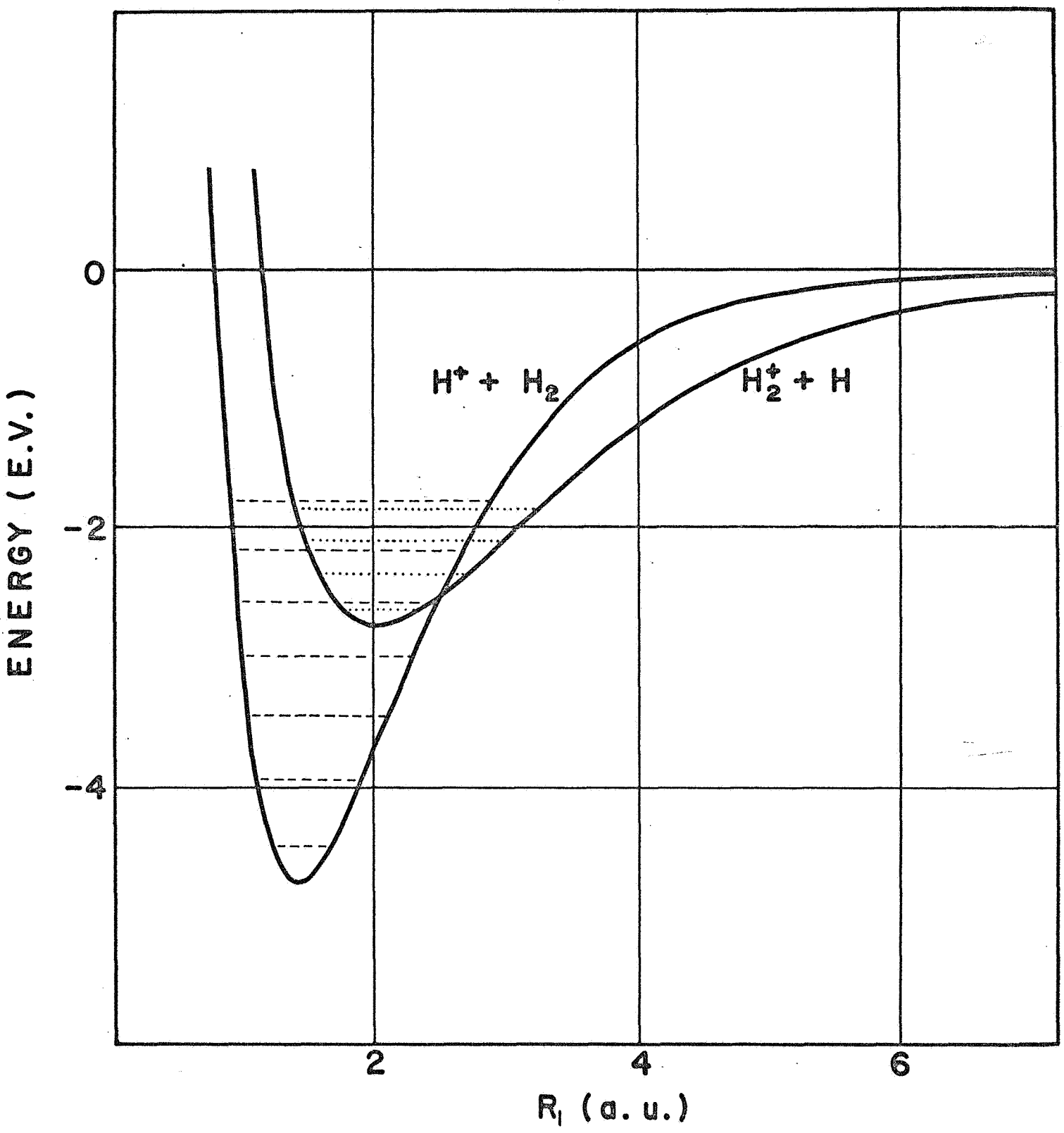
Fig. 3 Potential energy surface for the first excited singlet state of linear H_3^+.

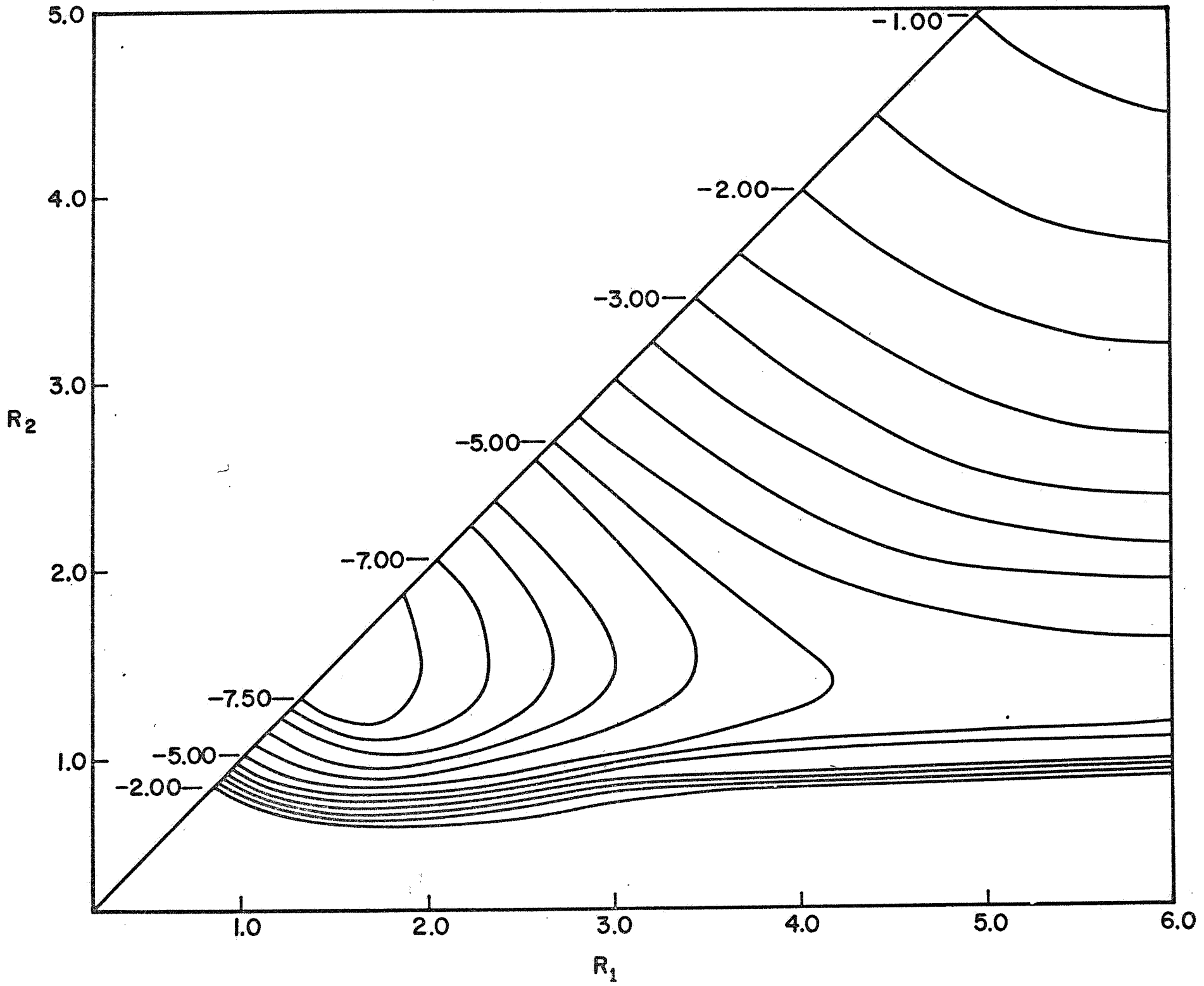
Fig. 4 Sections of the two lowest singlet surfaces of H_3^+, showing their avoided crossing.

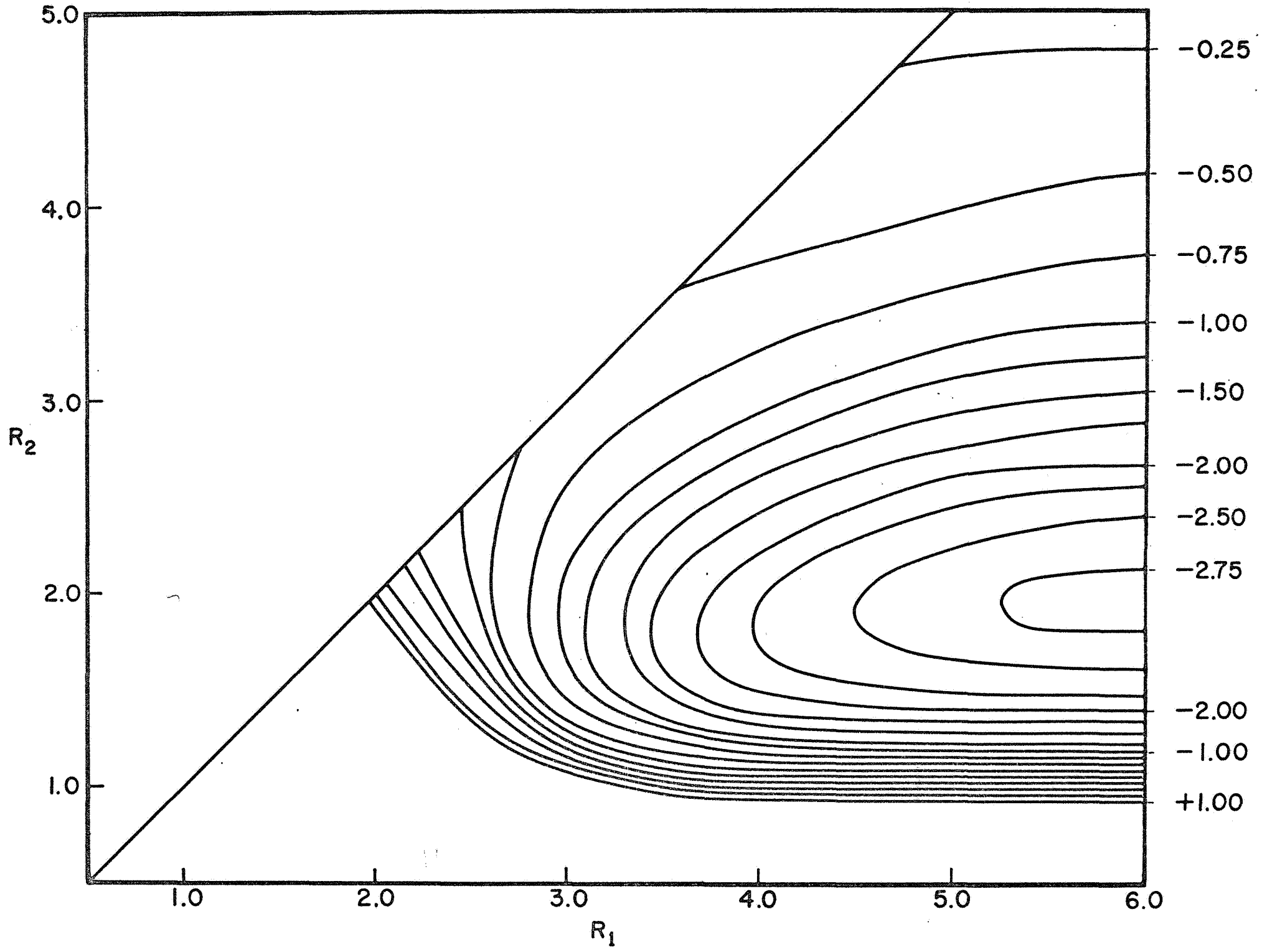
Fig. 5 Contour map of the non-adiabatic coupling terms for the linear symmetric vibrational mode. R_1, R_2 and the coupling matrix element are in a.u.

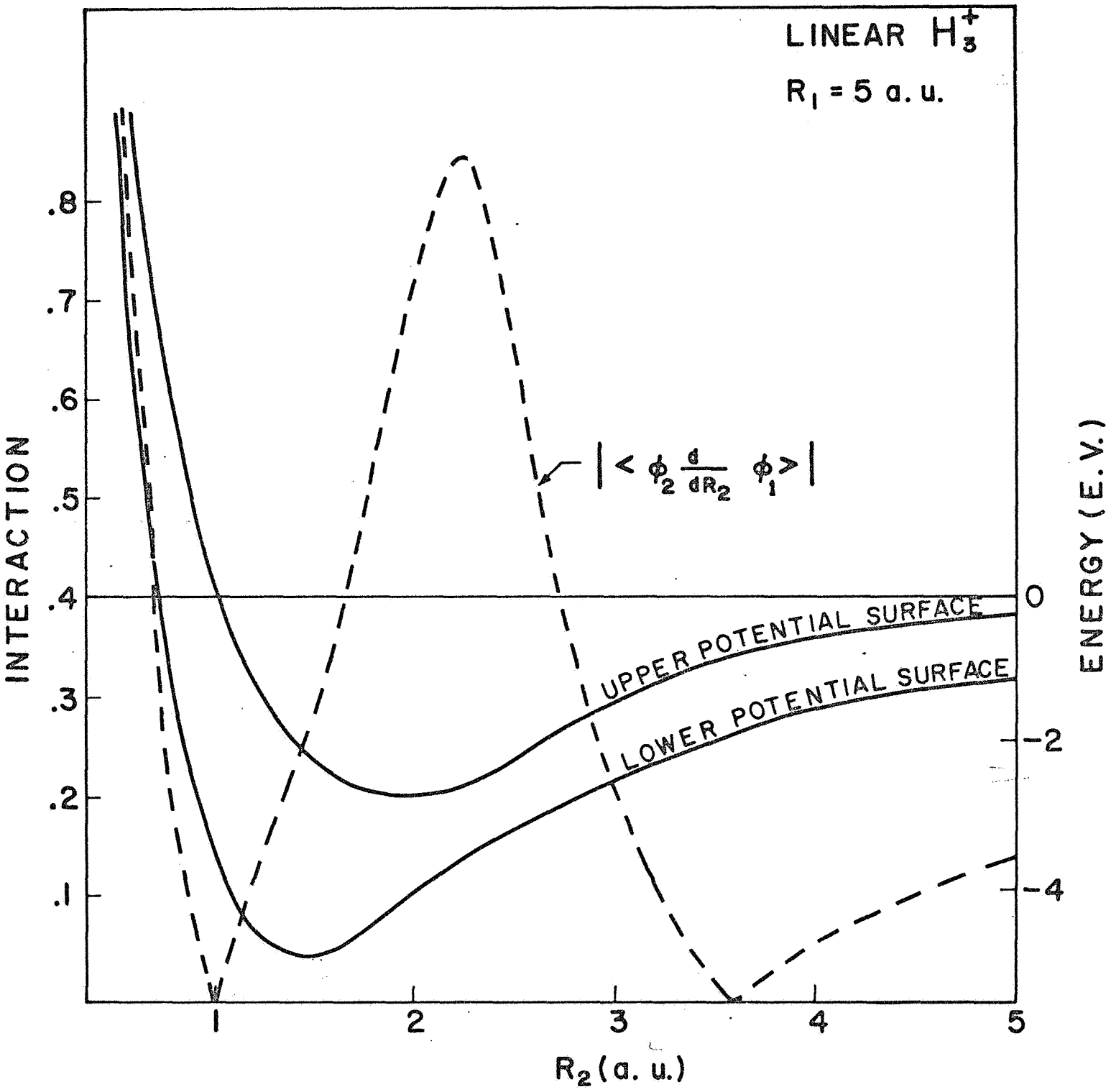
Fig. 6 Contour map of the non-adiabatic coupling terms for the linear asymmetric vibrational mode.

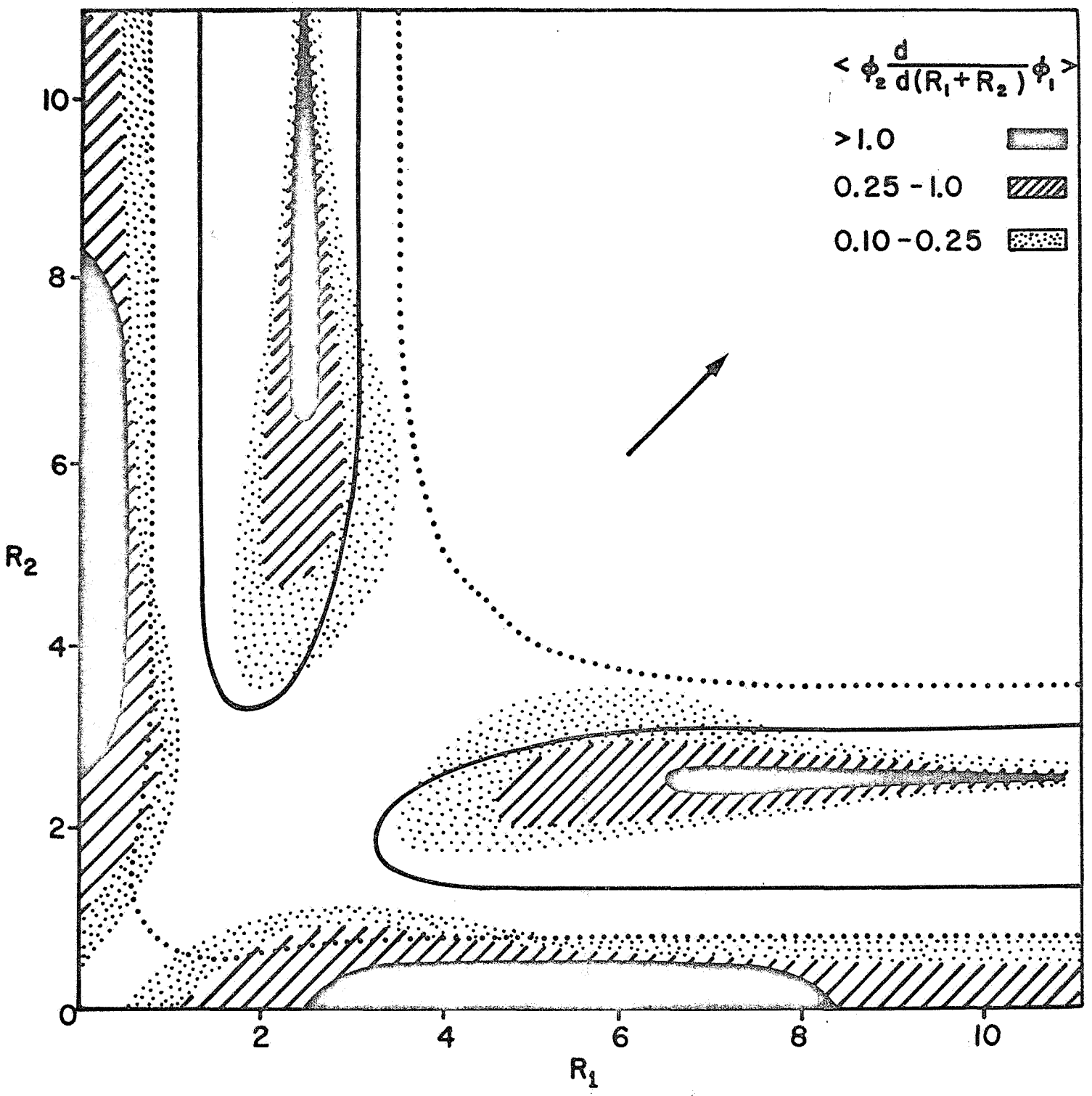
Fig. 7 Intensity of H_2^+ product formed in reaction (1) for initial collision energy of 2.88 eV. Solid line is experiment, dotted line is phase space prediction, and dashed line is phase space prediction with v=0 and v=1 levels omitted.

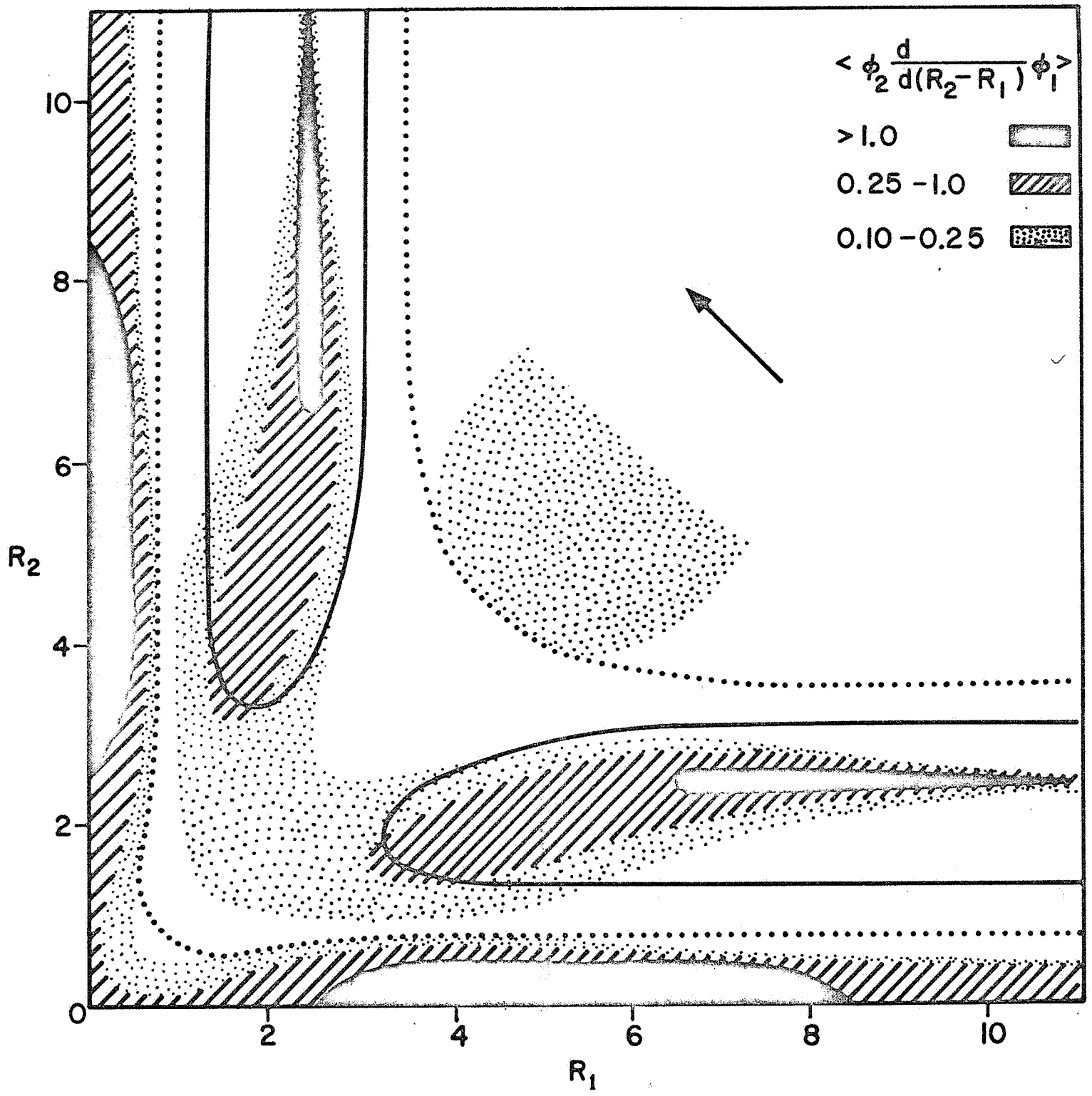

ENERGY (E.V.)
0
-2
-4
2
4
6
$H^+ + H_2$
$H_2^+ + H$
R_1 (a. u.)

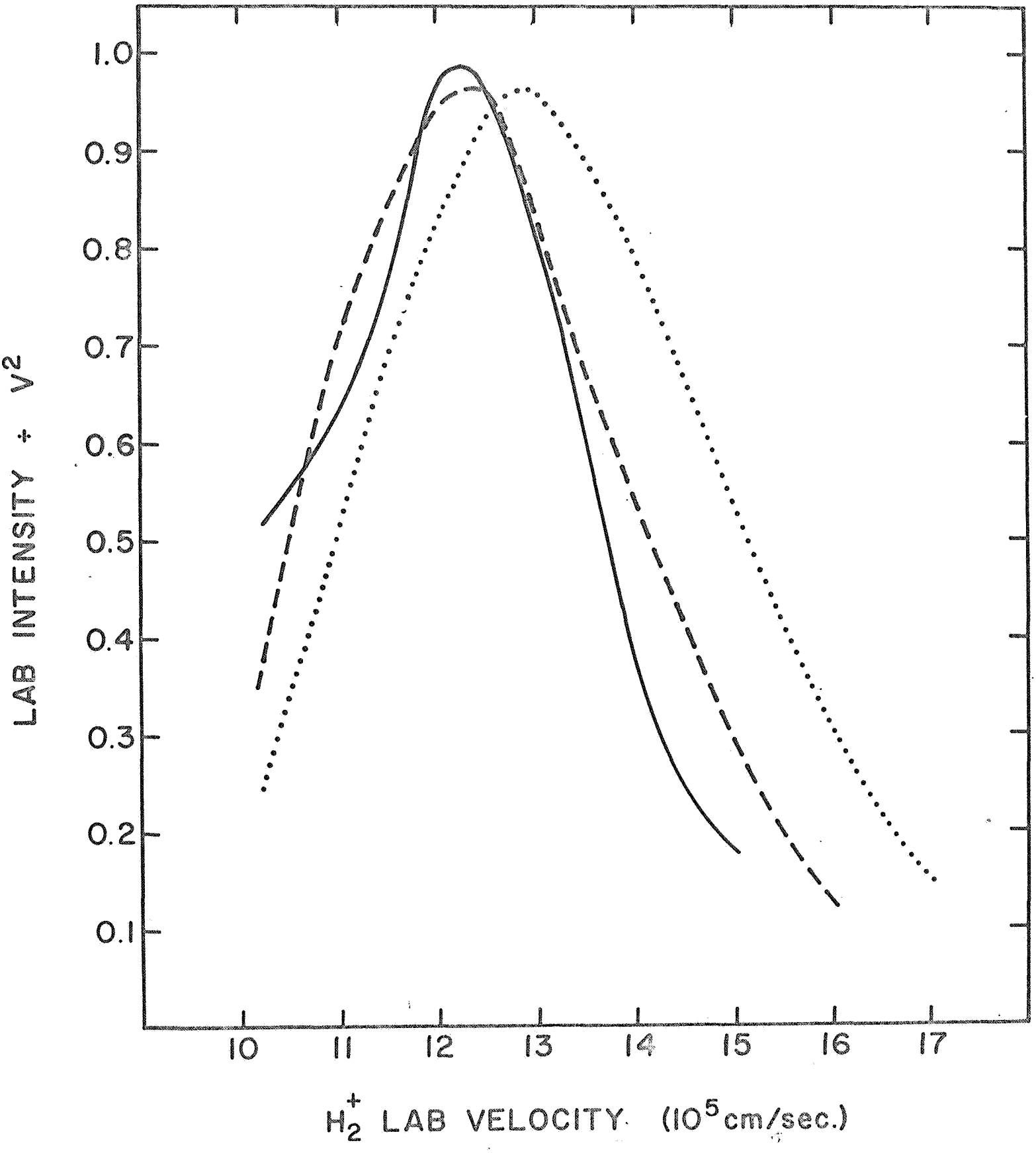

5.0
4.0
3.0
2.0
1.0
R2
-1.00
-2.00
-3.00
-5.00
-7.00
-7.50
-5.00
-2.00
1.0
2.0
3.0
4.0
5.0
6.0
R1


5.0
4.0
3.0
2.0
1.0
R_2
1.0
2.0
3.0
4.0
5.0
6.0
R_1
−0.25
−0.50
−0.75
−1.00
−1.50
−2.00
−2.50
−2.75
−2.00
−1.00
+1.00


LINEAR H_3^+
$R_1 = 5$ a. u.
$\left| \langle \phi_2 \frac{d}{dR_2} \phi_1 \rangle \right|$
UPPER POTENTIAL SURFACE
LOWER POTENTIAL SURFACE
INTERACTION
ENERGY (E.V.)
R_2 (a. u.)
.8
.7
.6
.5
.4
.3
.2
.1
0
-2
-4
1
2
3
4
5


$\langle \phi_2 \frac{d}{d(R_1+R_2)} \phi_1 \rangle$
>1.0
0.25 - 1.0
0.10 - 0.25
10
8
6
4
2
0
R_2
2
4
6
8
10
R_1


$\langle \phi_2 \frac{d}{d(R_2-R_1)} \phi_1 \rangle$
> 1.0
0.25 - 1.0
0.10 - 0.25
10
8
6
4
2
0
R_2
2
4
6
8
10
R_1


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
LAB INTENSITY ÷ V²
10
11
12
13
14
15
16
17
H₂⁺ LAB VELOCITY (10⁵cm/sec.)